Identification of General Unknowns

1 Scope

These procedures describe the general process for the analysis of general unknowns. These procedures are suitable for bulk samples which are not able to be analyzed by another explosives analysis Standard Operating Procedure (SOP). These procedures apply to caseworking personnel conducting work in explosives chemistry analysis.

2 Introduction

General unknowns include substances which are of indeterminate origin. Analytical approaches to an unknown substance will vary depending on the physical state and the quantity of the substance. In addition, information furnished by the contributor, as well as specific requests by the contributor, may indicate the appropriate methods for examining the unknown. Redacted

Where comparison samples are available, comment should be made regarding the consistency of the unknown with the comparison sample.

Unknown samples are examined visually prior to analysis. Physical and instrumental techniques which may include chemical tests, ion chromatography, infrared spectroscopy, liquid or gas chromatography/mass spectrometry, pH testing, polarized light microscopy, Raman spectroscopy, scanning electron microscopy/energy dispersive X-ray spectroscopy, solids probe mass spectrometry, solubility testing, thermal susceptibility tests, and X-ray diffraction may be employed to help identify a material.

3 Equipment/Materials/Reagents

Equivalent equipment, materials, and reagents may be substituted as needed.

3.1 Equipment

- Gas chromatograph with flame ionization detector (GC/FID)
- Fourier transform infrared (FTIR) spectrometer with attenuated total reflectance (ATR) or microscope attachment
- Gas chromatograph with mass spectrometer (GC/MS)
- Headspace gas chromatograph with mass spectrometer (HS-GC/MS)
- Ion Chromatograph (IC)
- Liquid chromatograph with mass spectrometer (LC/MS)
- Microscope (optical or digital) with optional digital camera

- Polarized light microscope (PLM)
- Raman spectrometer with macro compartment or microscope attachment
- Scanning electron microscope with energy dispersive X-ray spectrometer (SEM/EDS)
- Solids probe mass spectrometer (MS)
- Ultra performance liquid chromatograph with mass spectrometer (UPLC/MS)
- X-ray diffractometer (XRD)

3.2 Materials

- Autosampler vials and caps
- Hammer
- Kraft paper
- Lighter, torch, or matches
- Probe cups
- Solid phase microextraction (SPME) fibers
- Test strips (e.g., pH, peroxide, water-finding)
- Various disposable glassware and plasticware

3.3 Reagents/Solvents/Reference Materials

- Deionized water (18.2 MΩ)
- Diacetone diperoxide (DADP) and triacetone triperoxide (TATP)
- Hexane (reagent grade)
- Isopropyl alcohol (70% commercial product)
- Methanol (HPLC grade)
- Various solvents, as needed

4 Standards and Controls

All reference materials and reagents will be verified prior to, or in concurrence with, use in casework. Refer to the Verification of Reagents and Solvents SOP, the Verification of Reference Materials SOP, and the Records of Items Used As Known Materials SOP. Refer to the Instrument Parameters and Reagent Preparation SOP for information regarding the components and preparation of all standards and controls.

5 Sampling

Refer to the Sampling Procedures SOP in the Explosives Quality Assurance Manual.

6 Procedure

Explosives chemistry personnel will:

Clean work surfaces thoroughly with an isopropyl alcohol solution or other appropriate solvent. Cover the clean work surface with a disposable material such as kraft paper. Refer to the Explosives Contamination Prevention Guidelines for additional details.

Use appropriate personal protective equipment (e.g., safety glasses, laboratory coat, disposable gloves) when examining evidence. This is intended to protect personnel conducting the examination and to prevent contamination of evidence.

Review and understand all safety information contained in Section 10 prior to beginning the following procedures.

For each instrumental technique, refer to the Instrument Parameters and Reagent Preparation SOP for Performance Monitoring Protocol (PMP) information, instrument usage procedures, parameters, and reagent preparation information. Prior to evidence analysis, follow the PMP for the instrument to conduct a QA/QC check to verify the instrument's reliability and reproducibility from analysis to analysis.

6.1 Perform a visual (including microscopic examination) inspection to determine physical state, color, and consistency of the unknown.

6.2 Note the odor of the unknown if it is readily apparent.

6.3 An impact sensitivity test may be conducted to determine impact and friction sensitivity of the unknown.

6.4 A thermal sensitivity (flame) test may be conducted to determine sensitivity to flame or heat. Note results such as ease of ignitability, flame color, smoke, sound, and residue.

6.5 If there is a sufficient amount of sample, miscibility/solubility tests may be performed on the unknown using both aqueous and nonaqueous solvents. Refer to the Slurries, Emulsions, and Water Gels Analysis SOP for further guidance.

6.6 For an aqueous solution determine the pH. pH testing may also be conducted on a surface by applying moistened pH paper against it. Other colorimetric tests (e.g., peroxide test strips, water-finding paper) may also be used for presumptive testing. Verify the test works as designed using an appropriate positive control (e.g., acid/base, hydrogen peroxide, water).

6.7 Samples in an aqueous solution may also be analyzed by IC for anions and cations.

6.8 Physical or chemical separation of components may be indicated based on the visual exam and/or instrumental analysis results. Various solvents may be used to extract and isolate components for analysis.

6.9 FTIR or Raman analysis may be used to determine or confirm components of unknown mixtures or general classes of components in mixtures. Components should be compared to entries in reference libraries (e.g., Sadtler IR, Explosives Library). Commercial products may also serve as comparisons.

6.10 Unknown solids and residues of evaporated liquids may be analyzed by SEM/EDS for elemental components.

6.11 Crystalline solids may be suitable for XRD analysis.

6.12 Samples that are sufficiently volatile may be analyzed by GC/MS in electron ionization (EI) or chemical ionization (CI) modes. Prepare an approximately 500 ppm solution of the sample in a suitable solvent. Results may be compared to spectra in the National Institute for Standards and Technology (NIST) Library, Wiley Library, and/or to a reference or known material.

6.13 Samples of low volatility may be analyzed by solid probe mass spectrometry. A small portion of sample is transferred to a probe cup for analysis. Reference spectra may be obtained from reference or known materials.

6.14 Samples may be analyzed on the Headspace GC/MS using a heated headspace needle for volatile compounds. A 0.5 mL sample of the Redacted in an autosampler vial may serve as a positive control. A sealed blank autosampler vial serves as a negative control. The evidence may be heated prior to headspace sampling, based on the individual's judgment on how much heating is necessary and for how long. Ambient temperature or gentle heating may be sufficient.

6.15 Samples may be analyzed on the Headspace GC/MS for volatile compounds. A few grains of Redacted in an autosampler vial may serve as a positive control. A sealed empty autosampler vial serves as the blank. The evidence may be heated prior to headspace sampling, based on the individual's judgment as to how much heating is necessary and for how long. Ambient temperature or gentle heating may be sufficient.

6.16 For samples suspected of containing Redacted a hexane extract may be used to determine their composition. Prepare a hexane extract of the material, a hexane blank, and appropriate positive controls. Analyze the extracts by GC/FID.

6.17 Samples of high volatility, binary explosives, or combination Redacted

6.18 Samples may be analyzed by LC/MS (ESI or APCI configurations). Prepare an approximately 500 ppm solution in a suitable solvent. The extract may be diluted to coincide with instrument response. Results may be compared to the spectrum of a reference or known material. This method is especially suitable for samples subject to thermal degradation.

6.19 Samples may be analyzed by UPLC/MS. Prepare an approximately 0.5 ppm solution in a suitable solvent. This solution is generally diluted using a 50:50 mixture of methanol:deionized water. Be careful not to inject an overconcentrated sample into the UPLC/MS. Results may be compared to the spectrum of a reference or known material. This method is especially suitable for samples subject to thermal degradation.

6.20 If in the course of analysis it is determined that an unknown can be classified among materials analyzed by another explosives SOP, further analysis should be conducted according to the appropriate procedures.

7 Calculations

Not applicable.

8 Measurement Uncertainty

Although infrequent, the mass of a crude material may be requested by the contributor. When requested, refer to the Administrative Structure and Operating Guidelines SOP for information regarding measurement uncertainty of these results.

9 Limitations

Redacted

10 Safety

Safety protocols, contained within the FBI Laboratory Safety Manual, will be observed at all times.

Standard precautions will be taken for the handling of all chemicals, reagents, and standards including standard universal precautions for the handling of biological and potentially hazardous materials. Refer to the FBI Laboratory Safety Manual for proper handling and disposal of all chemicals. Personal protective equipment will be used when handling any chemical and when performing any type of analysis.

The handling of some explosive materials is hazardous due to potential ignition by heat, shock, friction, impact, or electrostatic discharge. Personnel should work with small quantities (such as a few grams) and properly store larger quantities in approved containers.

Dark materials may pose a hazard when being analyzed by Raman spectroscopy as they may be initiated by the laser. If this technique will be utilized, then the smallest possible sample amount should be used to minimize the risk. The laser power may also be decreased to avoid initiation.

11 References

FBI Laboratory Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

FBI Laboratory Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

FBI Laboratory Safety Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

Explosives Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

Explosives Standard Operating Procedures: Chemistry, Federal Bureau of Investigation, Laboratory Division, latest revision.

Instrument Operations Manuals for the specific models and accessories used.
Budavari, Susan, editor, *Merck Index*, 12th edition, Merck and Co., Inc.: Whitehorse Station, NJ, 1996.

Eckroth, David, editor, *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Wiley-Interscience: New York, 1984.

Gosselin, Robert E., Smith, Roger P., and Hodge, Harold C., *Clinical Toxicology of Commercial Products*, 5th edition, Williams and Wilkins: Baltimore, 1984.

Lewis, Richard J., editor, *Hawley's Condensed Chemical Dictionary,* 12th edition, Van Nostrand Reinhold: New York, 1993.

Rev. #	Issue Date	History
5	06/15/2020	Removed SPME fiber and updated negative control in section 6.15. Removed standards list from section 4. Updated section 8.
6	07/15/2020	Updated SOP title in section 6.17.

Approval

Redacted - Signatures on File

Explosives Unit Chief Date: 07/14/2020

TL Approval

Explosives Chemistry
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